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Facile Synthesis of High-Quality, Water-Soluble, Near-Infrared-Emitting PbS Quantum Dots

Dawei Deng,*[a] Wenhao Zhang,[b] Xinyang Chen,[a] Fei Liu,[a] Jian Zhang,[a] Yueqing Gu,*[a] and Jianming Hong[c]

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PbS quantum dots (QDs) with strong near-infrared (NIR) fluorescence have been prepared directly in aqueous solution, by using dihydrolipoic acid (DHLA) as a stabilizer. The photoluminescence (PL) emission maximum could be tuned conveniently over a wide range (from ca. 870 nm to 1010 nm) by manipulating the experimental conditions, such as the Pb/S or DHLA/Pb molar ratios. Under optimized conditions, the maximum PL quantum yield was approximately 10 %. These resultant PbS QDs were highly stable when stored in the dark at 4 °C. After one month of storage, the PL emission intensity decreased by only about 20 %, and no obvious spectral redshift was observed. We scaled up further the synthesis of PbS QDs in the lab, where the concentration of QDs was increased to 8 mM from the usual 1 mM. The experimental results from transmission electron microscopy (TEM) imaging, selected area electron diffraction (SAED), and powder X-ray diffractometry (XRD) analyses indicated that the as-prepared PbS QDs had an extremely small diameter (less than 4 nm) and exhibited a face-centered cubic crystal structure. Such aqueous quantum dots are considered to have tremendous applications in biomedical imaging and the fabrication of nanoscaled devices because of their low toxicity, strong fluorescence, excellent water-solubility, stability, and biological compatibility relative to other highly toxic thiol (3-mercaptopropionic acid) stabilized NIR-emitting QDs (such as CdTe, CdHgTe, HgTe).

Introduction

Due to quantum confinement effects, semiconductor quantum dots (QDs) or nanocrystals exhibit special physical and chemical properties that are greatly different from those of their corresponding bulk form.[1–4] Over the past two decades, great efforts have been invested into the synthesis of highly fluorescent semiconductor quantum dots.[5–11] Among them, the near-infrared(NIR)-emitting QDs with emission wavelengths between 700 and 1000 nm are of particular interest to researchers, because the autofluorescence and absorption from most flesh tissues are lowest in this range.[12–14]

To date, various kinds of NIR-emitting QDs have been synthesized by organometallic routes or aqueous methods.[15–25] Although quantum dots (such as InP, InAs, and CdTe/CdSe) with tunable size and good optical properties have been obtained by an organometallic method,[15–17] the drawbacks of these approaches were the use of organic solvents and high reaction temperature. Furthermore, for biological applications, those NIR-emitting QDs need to undergo surface modification with hydrophilic capping agents in aqueous solution. However, the surface modification may decrease the PL emission of the QDs, which is highly sensitive to the surface properties.[26,27] Thus, it would be more desirable to devise a facile aqueous synthetic route to the QDs with good water-solubility. Currently, the QDs with NIR fluorescence synthesized in aqueous solution include mainly CdTe,[18] CdTe/CdS,[19] CdTe/CdSe,[20] CdTe/ZnS,[21] CdHgTe,[22] CdHgTe/CdS,[23] CdHgTe/ZnS,[21] HgTe,[24] and HgTe/CdS.[25] To the best of our knowledge, these Cd-, Hg-, Te-, and Se-based quantum dots all are highly toxic. Moreover, 3-mercaptopropionic acid (MPA), the only known stabilizer used in synthesizing these NIR-emitting QDs, is also a toxic carcinogenic substance with an awful odor.[18,21,23] These fatal shortcomings will deter the application of these QDs in biomedical fields.

Compared with the materials described above, PbS has relatively low toxicity, and in view of the small band gap (0.41 eV) and large exciton Bohr radius (18 nm),[28] PbS should also be very suitable for synthesizing NIR-emitting nanocrystals. However, in previous reports on PbS, most of the synthetic efforts yielded irregularly shaped PbS nanocrystals;[29] few synthetic approaches were carried out to prepare spherical PbS QDs,[30–33] especially water-soluble

[a] Department of Biomedical Engineering, School of Life Science and Technology, China Pharmaceutical University, Nanjing 210009, P. R. China
E-mail: david597300@163.com
guyueqing@hotmail.com
[b] School of Chemistry and Chemical Engineering, Key Laboratory of Analytical Chemistry for Life Science (Ministry of Education of China), Nanjing University, Nanjing 210093, P. R. China
[c] Center of Material Analysis, Nanjing University, Nanjing 210093, P. R. China

spherical PbS QDs.[34] So far, only the group of Kumacheva succeeded in synthesizing highly luminescent PbS QDs in aqueous medium, by using a mixture of thioglycerol (TGL) and dithioglycerol (DTG) as the capping agents, which indicates that the direct aqueous synthesis of PbS QDs is very difficult because of the lack of suitable stabilizers.[34] Furthermore, the resulting water-soluble PbS nanocrystals exhibited emission in the range 1000–1400 nm, the facile and environmentally friendly aqueous synthesis of small PbS QDs with a band gap in the range 700–1000 nm still being challenging.

In the past five years, we have been developing the facile and environmentally friendly approach for the synthesis of high-quality semiconductor nanomaterials,[35] because the final purpose of the research in nanoscience is to apply these materials in industry and daily life, although this still is a huge challenge. As a continuation, in this manuscript, we report a new facile, one-pot approach to high-quality, water-soluble PbS QDs with strong NIR fluorescence in the range ca. 870–1010 nm. This ready synthesis was carried out in water under ambient conditions (at room temperature without the need for the protection of an argon or nitrogen atmosphere), by using nontoxic DHLA [$HSCH_2CH_2CH(SH)(CH_2)_4COOH$, a vitamin essential for life] as a stabilizer. To the best of our knowledge, the DHLA-based capping was only used to produce CdSe-ZnS and CdTe QDs before.[36] We explored systematically the influences of the precursor Pb/S molar ratio, the DHLA/Pb molar ratio, and the pH of the original solution on optical properties, storage stability at 4 °C, and the scale-up of the synthesis of PbS QDs in the lab. We also investigated in detail the morphology and crystal structure of as-synthesized water-soluble PbS QDs by using a combination of TEM, SAED, and XRD. Here, it should be mentioned that, relative to the previous aqueous synthetic approach of PbS QDs [the stabilizers (TGL and DTG) are all toxic volatile liquids with an awful odor; the PL emission of the resulting QDs is in the range 1000–1400 nm; the terminal group of the ligand molecules on the QD surfaces is –OH, and the QDs are synthesized under strong alkaline conditions (pH = 11.2)],[34] our strategy is more facile and environmentally friendly, and the resulting NIR-emitting PbS QDs should be more promising in biological applications (the stabilizer DHLA is nontoxic and contains a –COOH terminus); the PL emission of the resulting QDs is in the range 870–1010 nm, and the QDs can be prepared in weak alkaline solution (pH = 8.0).

Results and Discussion

Synthesis of Water-Soluble, NIR-Emitting, DHLA-Stabilized PbS QDs and the Reaction Conditions

The detailed synthetic steps of DHLA-stabilized PbS QDs are described in the Experimental Section. When the solution of Na_2S was slowly added dropwise to the system (pH = 9.0) containing 0.1 mmol Pb^{2+} ions and 0.3 mmol DHLA, the initial solution turned from pale yellow to dark-brown instantly, indicating the formation of PbS QDs. Figure 1 shows the absorption and PL spectra of the as-prepared DHLA-stabilized PbS QDs. Compared with bulk PbS (the band gap energy for bulk-phase PbS is 0.41 eV; λ_{max} = 3020 nm), the PL peak (at 935 nm) and absorption shoulder are vastly blueshifted and finally in the near-infrared spectral region, which provides evidence for the strong effect of quantum confinement. These experimental results demonstrate clearly that water-soluble, NIR-emitting PbS QDs can be prepared by using DHLA as a capping agent, in addition to the mixture of thioglycerol (TGL) and dithioglycerol (DTG) reported previously. Compared to TGL and DTG (they are toxic liquids with an irritating odor), DHLA [$HSCH_2CH_2CH(SH)(CH_2)_4COOH$] is nontoxic and contains a -COOH terminus, which may make the NIR-emitting DHLA-stabilized PbS QDs more promising in biological applications.

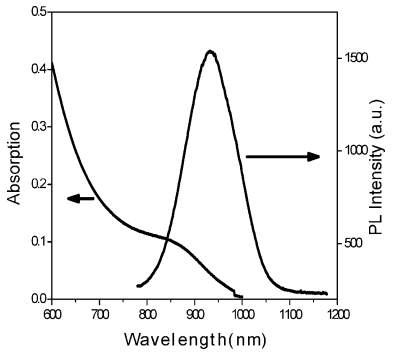

Figure 1. Absorption and PL spectra of the as-prepared DHLA-stabilized PbS QDs.

Having demonstrated the feasible synthesis of NIR-emitting PbS QDs in water solution, which was the primary goal of this work, we next explored systematically the influence of various experimental variables, including the precursor Pb/S molar ratio, the DHLA/Pb molar ratio, and the pH of the original solution, on optical properties. Figure 2 shows the PL and absorption spectra of DHLA-stabilized PbS QDs obtained at various precursor Pb/S molar ratios, where the concentrations of DHLA and Pb^{2+} ions were set to 6 mM and 2 mM, respectively, and only the added molar amount of Na_2S (the sulfur source of PbS QDs) was varied. In Figure 2A, the emission peak redshifted from 905 to 1010 nm when the Pb/S molar ratio was decreased from 1:0.2 to 1:0.8, which corresponds to QD diameters from approximately 2.3 to 4.0 nm according to the TEM characterization. The PL intensity reached a maximum at the Pb/S molar ratio 1:0.4. Similarly to PL spectra, the absorption spectra presented in Figure 2B also redshifted correspondingly. These experimental results may indicate that a section of the newly formed PbS particles, by the reaction between the successively introduced S^{2-} anions and the Pb^{2+} ions, in the present synthetic system will deposit on the surface of the initially formed small PbS "core" QDs, resulting in the symmetrical increase in the size of the quantum dots.

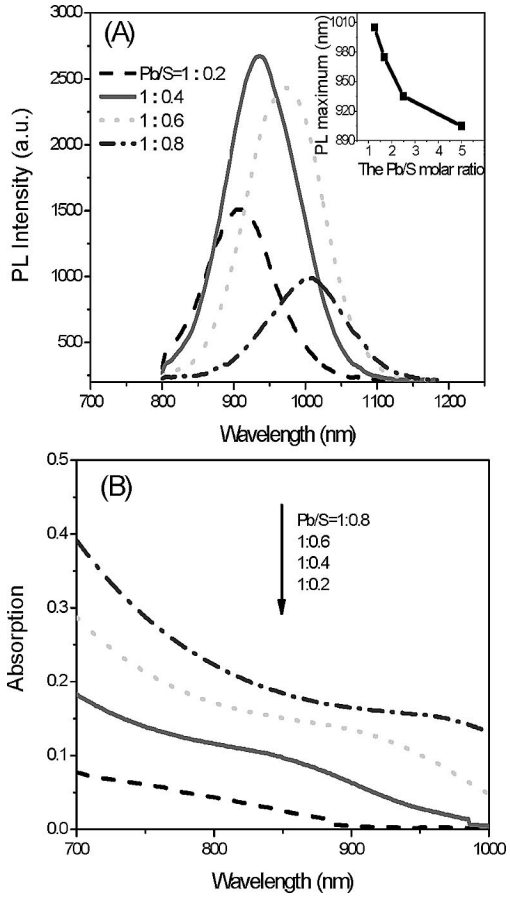

Figure 2. PL (A) and absorption (B) spectra of DHLA-stabilized PbS QDs with different sizes, obtained by changing the precursor Pb/S molar ratio. The inset of A shows the PL peak position as a function of Pb/S molar ratio.

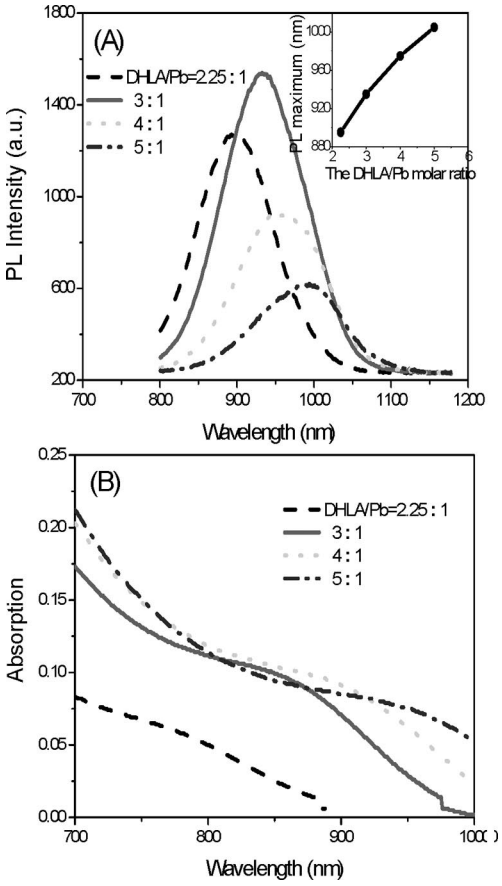

Figure 3. PL (A) and absorption (B) spectra of DHLA-stabilized PbS QDs with different sizes, obtained by changing the DHLA/Pb molar ratio. The inset of A shows the PL peak position as a function of DHLA/Pb molar ratio.

The DHLA/Pb molar ratio was also observed to influence the optical properties of PbS QDs, when the concentration of Pb^{2+} ions was fixed at 2 mM and the Pb/S molar ratio was set to 1:0.5. As shown in Figure 3, while increasing the DHLA/Pb molar ratio, both the PL peak and the absorption shoulder of PbS QDs redshifted, which indicated the increase in size of the QDs. In the process of quantum dot preparation, we observed that, when the DHLA/Pb molar ratio was less than 2.25:1, the resulting PbS QDs were not stable and would precipitate after about two days of storage at room temperature. However, when the DHLA/Pb molar ratio was more than 5:1, the as-synthesized PbS QDs showed poor near-infrared fluorescence. Hence, the DHLA/Pb molar ratio 3:1 is optimal for the preparation of water-soluble, NIR-emitting PbS QDs. Under these conditions, the PL quantum yield is about 9.7%.

In the inset of Figure 3A, the effect of the DHLA/Pb molar ratio on the PL peak is further demonstrated: the wavelength of the PL emission shifted from 895 to 1000 nm upon tuning the DHLA/Pb molar ratio from 2.25:1 to 5:1. We explain this effect as follows: In an alkaline solution, sulfur atoms of DHLA are deprotonated and can react subsequently with Pb^{2+} ions to form the complexes $[PbDHLA]^-$, $[Pb(DHLA)_2]^{4-}$, and $[Pb(DHLA)_3]^{7-}$, by a reaction similar to that between DTG and Pb^{2+} ions.[34] The concentration of each complex in the solution depends strongly on the DHLA/Pb molar ratio: on increasing the DHLA/Pb molar ratio, the concentration of $[Pb(DHLA)_3]^{7-}$ will increase, and correspondingly, the concentrations of $[PbDHLA]^-$ and $[Pb(DHLA)_2]^{4-}$ will decrease. Upon addition of S^{2-} ions, $[PbDHLA]^-$ and $[Pb(DHLA)_2]^{4-}$ will participate in the nucleation of QDs. By contrast, in the case of $[Pb(DHLA)_3]^{7-}$, the Pb center does not react readily with S^{2-} ions, since its six orbitals participate in bond formation with ligands. Thus, $[PbDHLA]^-$ and $[Pb(DHLA)_2]^{4-}$ should favor the formation of QD nuclei, whereas $[Pb(DHLA)_3]^{7-}$ serves only as a feeding material. Hence, at higher DHLA/Pb molar ratio, a smaller number of PbS nuclei are formed, and as a result, the quantum dots synthesized have a larger size.

In the present study, the influence of the pH of the original solution on the optical properties of DHLA-stabilized PbS QDs was also investigated further, and the obtained experimental results are shown in Figure 4. Here, the solution pH was adjusted to 8.0, 9.0, 10.0, and 11.2 with 0.2 M NaOH solution, and all optical spectra were measured under the same conditions. As shown in Figure 4A, when the pH was varied from 8.0 to 10.0, the PL peak red shifted

gradually from 890 to 937 nm. However, if the solution pH was further increased up to 11.2, the PL spectrum of the QD dispersion did not show significant changes. A similar evolution trend was observed in the absorption spectra of these QDs in Figure 4B. Here, we suppose that, when the DHLA/Pb molar ratio is fixed, the higher the pH of the original solution is, the easier the formation of the lead(II)–DHLA complexes. Thus, at higher pH, a smaller number of PbS nuclei are formed, resulting in the increase of the QD size and the corresponding redshift of the spectrum. However, if the pH of the original solution exceeds 10.0, the influence of the pH of the original solution on the optical properties will become weak.

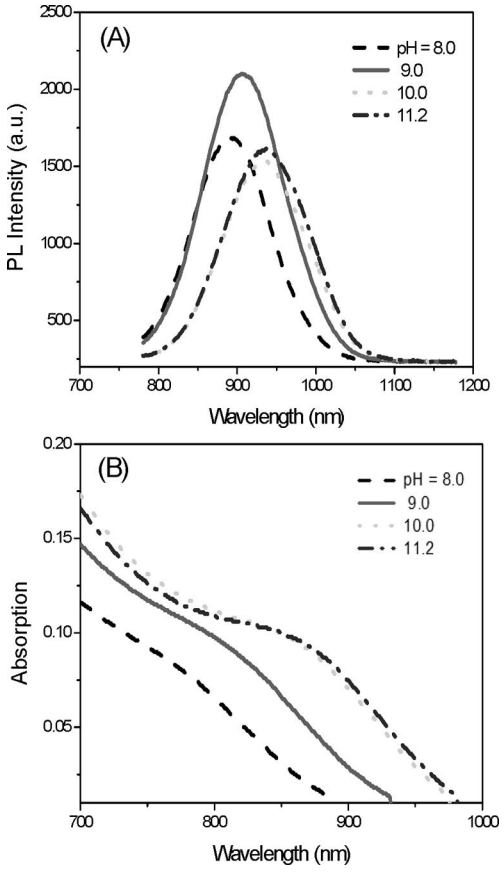

Figure 4. PL (A) and absorption (B) spectra of DHLA-stabilized PbS QDs obtained by changing the solution pH, where the precursor molar ratio of Pb/S/DHLA and the concentration of Pb^{2+} ions were fixed at 1:0.5:3 and 2 mM, respectively.

Although, compared to PbS QDs made at three other pH values, the QDs formed at pH 9.0 showed the strongest PL emission, the QDs produced at pH 8.0 still had highly desirable PL properties (the PL quantum yield was close to 10%). This experimental result indicates clearly that, by using DHLA as a stabilizer, high-quality, NIR-emitting PbS QDs can be prepared under weak alkaline conditions, namely pH = 8.0, which is close to the physiological pH. This is very significant for the future applications of quantum dots in biomedical fields, because in most of the previous studies,[9,10,18–25] thiol-stabilized nanoparticles can only be synthesized under strong alkaline conditions (such as pH = 11.2), including the thiol-capped PbS nanocrystals reported previously.[34]

The Scale-Up of the Synthesis of Water-Soluble, NIR-Emitting, DHLA-Stabilized PbS QDs

Typically, the concentration of PbS QDs produced was 1 mM (the concentration of PbS QDs refers to the sulfur concentration of QDs). With an eye to bioapplications in NIR fluorescence imaging, we attempted to scale up the synthesis of PbS QDs at pH 8.0. Here, the concentrations of PbS QDs was increased to 8 mM from the usual 1 mM, and the total volume of the original solution was increased to 200 mL from the usual 50 mL. Thus, in a single synthesis, we could obtain hundreds of milligrams (ca. 500 mg) of DHLA-stabilized PbS QDs. To determine their optical properties, all samples were diluted to the same concentration. Figure 5 displays the obtained PL and absorption

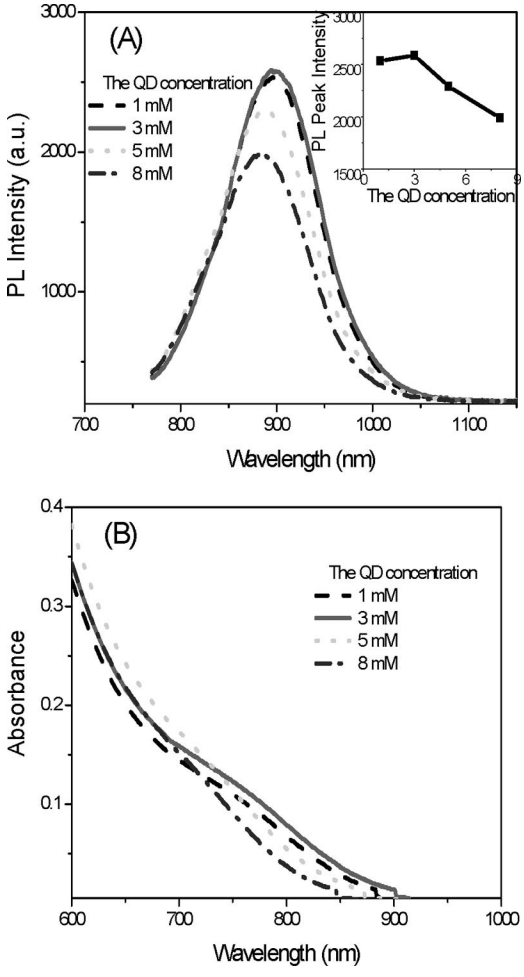

Figure 5. PL (A) and absorption (B) spectra of DHLA-stabilized PbS QDs obtained by changing the total concentrations of the precursors, where the precursor molar ratio of Pb/S/DHLA and the solution pH value were fixed at 1:0.5:3 and 8.0, respectively. In optical testing, all samples were diluted to the same concentration. The inset of A shows the PL peak intensity as a function of the QD concentration.

spectra of DHLA-stabilized PbS QDs prepared at different precursor concentrations. As presented in Figure 5A, for the quantum dots synthesized at an increased concentration of QDs of 8 mM, that is, eight times that in the procedures described above, the PL emission intensity has only a small decrease of approximately 23% relative to that of the QDs prepared at the optimal concentration, which was accompanied by a ca. 10 nm blue shift of the luminescence peaks of the dispersions. The absorption spectra in Figure 5B show a similar observation: PbS QDs produced at different precursor concentrations have similar optical properties. Hence, the experimental results in Figure 5 confirm fully that this synthesis can be scaled up, and, at the same time, also demonstrate that the present synthetic procedure is highly reproducible.

Storage Stability of As-Synthesized Water-Soluble, NIR-Emitting, DHLA-Stabilized PbS QDs

In this study, we investigated the storage stability of as-synthesized aqueous, NIR-emitting, DHLA-stabilized PbS QDs. Here, the resulting QD solutions were stored at 4 °C in the dark. Time evolutions of PL and NIR absorption spectra of PbS QDs stored at 4 °C in the dark are shown in Figure 6. After 30 days of storage, the PL emission intensity of the QD dispersions only decreased about 20%, the corresponding absorbance only increased slightly, and no obvious redshifts of the absorption shoulder and the PL peak were observed. These experimental results are very different from the previous report that the absorption shoulder and PL peak of PbS nanocrystals stabilized with a mixture of TGL and DTG redshift continuously with storage time (the PL peak changes from 1050 to 1400 nm).[34b] The little change in the optical properties during storage brings more convenience in applying these NIR-emitting PbS QDs in various fields. We noticed that, upon further prolonging the storage time, these PbS QDs precipitate gradually, because DHLA ligands are oxidized into lipoic acid, and no free DHLA ligands are available in solution. However, if sealed immediately after preparation or stored under a nitrogen atmosphere (i.e., reducing the periodical exposure to air during absorption and PL measurements), the quantum dots and their optical properties are be stable for at least about two months.

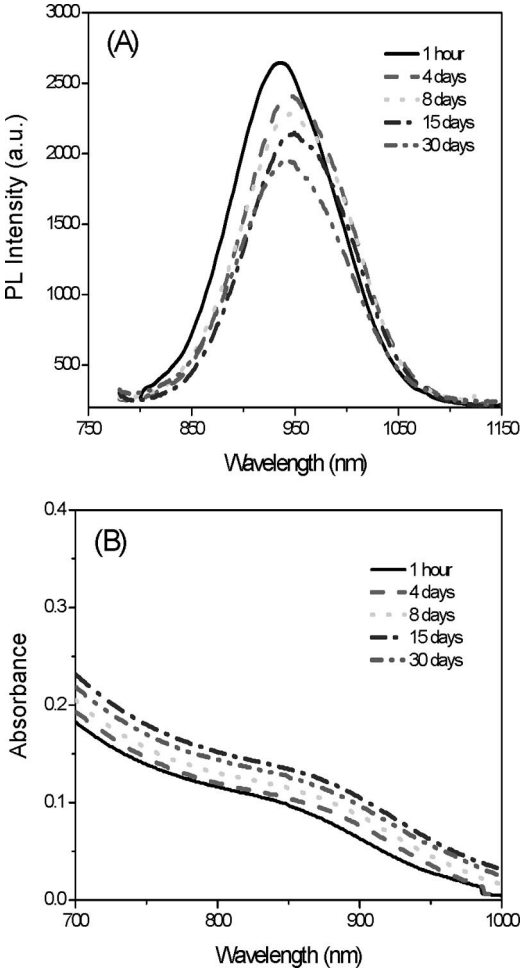

Figure 6. Time evolutions of the PL (A) and NIR absorption (B) spectra of PbS QDs stored at 4 °C in the dark. The precursor molar ratio of Pb/S/DHLA was 1:0.5:3.

Morphological and Structural Analyses of As-Synthesized Water-Soluble, NIR-Emitting, DHLA-Stabilized PbS QDs

A typical TEM image for the as-synthesized NIR-emitting, DHLA-stabilized PbS QDs (λ_{max} = 970 nm) is shown in Figure 7A. It is quite evident that these quantum dots have nearly spherical shape with good monodispersity and remain well separated. The corresponding average size is approximately 3.5 nm. Figure 7B displays the typical high-resolution TEM image of the NIR-emitting PbS QDs. The clear lattice fringes in the HRTEM image indicate that these quantum dots are nearly single-crystalline in structure, although they were synthesized at room temperature. The lattice spacing as labeled in Figure 7B is 0.29 nm, corresponding to the (200) plane of the cubic structure of PbS. Especially, for the single quantum dot marked by a white frame in panel B, the two lattice planes with an interplanar distance of 0.29 nm are perpendicular to one another. This experimental observation reveals more directly that these quantum dots are cubic PbS. In addition, the selected area electron diffraction (SAED) pattern in Figure 7C also shows them to be crystalline, and all diffraction spots can be assigned to cubic PbS.[33]

Figure 8 shows a typical X-ray diffraction pattern of the powdered PbS QDs stabilized by DHLA. All seven reflections matched well the reference powder diffraction pattern of PbS. The positions of these diffraction peaks demonstrate clearly that the resulting DHLA-stabilized PbS QDs have a cubic crystal structure. Thus, the experimental results from XRD measurements, HRTEM imaging, and SAED analysis are consistent, confirming the face-centered cubic structure of the produced PbS QDs.

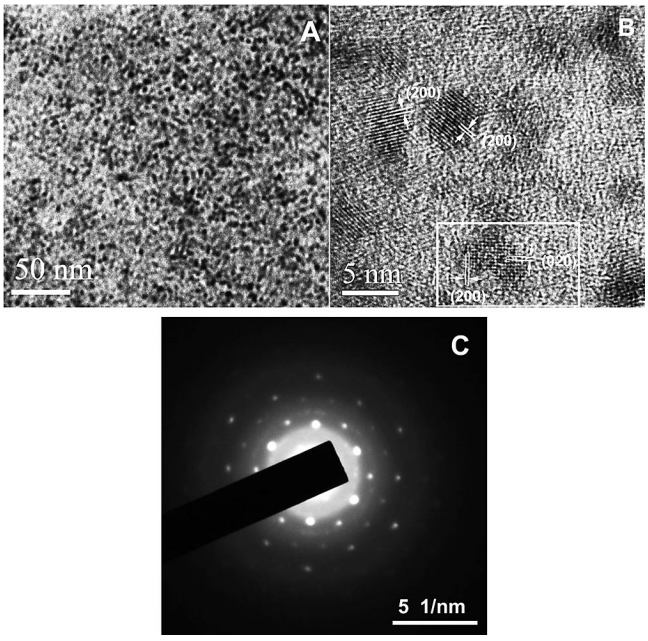

Figure 7. Typical TEM (A) and HRTEM (B) images of NIR-emitting, DHLA-stabilized PbS QDs (λ_{max} = 970 nm). (C) SAED pattern of PbS QDs.

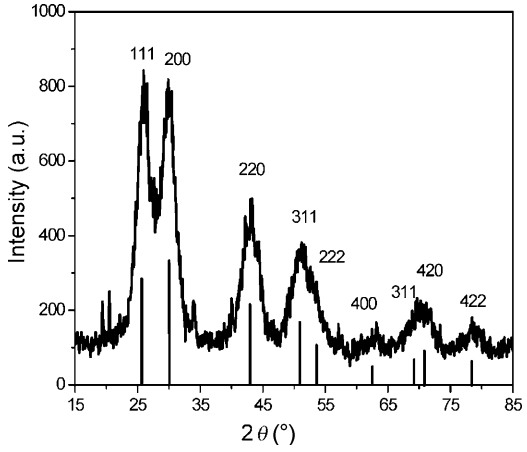

Figure 8. Typical XRD pattern of DHLA-stabilized PbS quantum dots (λ_{max} = 970 nm).

Conclusions

In summary, we have developed a facile and environmentally friendly one-pot approach to prepare water-soluble PbS QDs with strong fluorescence in the NIR spectral range ca. 870–1010 nm, by using DHLA as the stabilizer under ambient conditions within 30 min. The as-prepared DHLA-stabilized PbS QDs showed a high stability against aggregation when stored in the dark at 4 °C; their optical properties were almost intact after one to two months of storage. We succeeded in the scale-up of the synthesis of PbS QDs in the lab. Furthermore, we demonstrated systematically the morphology and the crystal structure of as-synthesized water-soluble PbS QDs by the TEM, SAED, and XRD techniques. The combination of low toxicity, strong fluorescence, and excellent water-solubility, stability, and biological compatibility makes these nanoparticles a promising material in optical devices and NIR fluorescence imaging, as compared to the highly toxic NIR-emitting QDs (such as CdTe, CdHgTe, HgTe) and the water-soluble PbS QDs synthesized previously.

Experimental Section

Chemicals: Lipoic acid (LA) (95+%), sodium borohydride (96+%), lead(II) acetate trihydrate (99+%), $Na_2S{\cdot}9H_2O$ (98+%), and sodium hydroxide (96+%) were of analytical grade and used as received. The water used in all experiments was deionized to a resistivity of 18.2 MΩ·cm.

One-Pot Synthesis of Water-Soluble, DHLA-Stabilized PbS Quantum Dots: The typical synthetic route to DHLA-stabilized PbS QDs is as follows: Firstly, an aqueous solution of DHLA was prepared with a simple reduction reaction of lipoic acid by sodium borohydride: in brief, under ambient conditions, at room temperature, deionized water (2 mL) was added dropwise to lipoic acid (62 mg) and excessive sodium borohydride (20 mg) with magnetic stirring. After the initial vigorous foaming subsided (about 3 min), an aqueous solution of DHLA was obtained. Secondly, the aqueous solution of DHLA (0.3 mmol) was adjusted to pH = 9 by adding NaOH dropwise (0.2 mol·L^{-1}). Then, lead(II) acetate solution (1 mL, 0.1 M) was introduced into the solution of DHLA with strong magnetic stirring. Finally, a solution of Na_2S (2 mL, 0.025 M) was slowly added dropwise to the system. The solution instantly turned from buff to dark-brown, indicating the formation of PbS QDs. Stirring was continued for 5 min. Generally, the typical time for the preparation of DHLA-stabilized PbS QDs is short and less than 30 min. Here, the total volume of original solution was 50 mL, and the initial molar ratio of Pb/S/DHLA was set to 1:0.5:3 unless otherwise specified.

Characterization: An S2000 eight-channel optical fiber spectrophotometer (Ocean Optics Corporation, America), and an NL-FC-2.0–763 semiconductor laser (λ = 765.9 nm, Enlight, China) light were utilized for the detection of fluorescence spectra. A 754-PC UV/Vis spectrophotometer (JingHua Technological Instrument Corporation, Shanghai, China) was used for measurement of UV/Vis spectra. All optical measurements were performed at room temperature. PL quantum yields of PbS QDs in water were calculated by comparing their integrated emission to that of a solution of cypate in aqueous DMSO (20%) solution (the absorption and PL emission peaks of cypate are at 790 nm and 810 nm, respectively; the PL quantum yield is 12%) supplied by Samuel Achilefu (Department of Radiology, Washington University at St. Louis). The pH meter (PHS-25) was purchased from Shanghai Scientific Instrument Corporation (Shanghai, China). A JEM-2100 transmittance electron microscope (JEOL, Japan) was used to evaluate the morphology and crystal structure of the quantum dots. The powder XRD measurement was carried out with a Philips X′Pert PRO X-ray diffractometer (λ = 1.54178 Å).

Acknowledgments

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